PREPARATION OF EFFICIENT CATALYSTS – ADSORBENTS FOR CLEANING OF GASES FROM SULFUR COMPOUNDS

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The process of cleaning of hydrocarbon gases by the concentrates of manganese natural ores (Chiatura deposit, Georgia) from sulfur compounds has been investigated. It was shown that critical sulfur content of the adsorbent mass in temperature range of 350-400 ^{0}C comprises 15-17 wt. %. The technology of preparation of pelletized oxide-manganese catalyst-adsorbent is proposed. The effect of the parameters of pelletizing process: compacting pressure, composition, type and properties of stabilizing components on formation of secondary structure was established. The data of activity and some physical-chemical characteristics of pelletized oxide-manganese catalyst-adsorbent are presented.

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Introduction

According to the data of publications of Energetic Informational Agency of USA Energetic Ministry: "Natural Gas Annual" and "International Energy Annual", all over the World nearly to 100 billion m^3 of gases are used annually, for chemical purposes, which consists 2,5-3 % of produced gas. This gas is mainly formed at oil deposits and is a valued raw material for gas refining factories. Along with it, it is well known that a major part of the reserves of natural gases is due to those deposits which involve sulfur compounds (preferentially in the form of hydrogen sulfide - H_2S) to a variable extent. There are a number of small and large oil deposits, in the oil-gas composition of which a concentration of H_2S is high and varies from 3.6 wt. % to 20-30 wt. %.[1-3] Respectively, a low rate of refining of such oil, condensate and gases may be explained by high content of sulfur compounds in them, which causes a damage of buildings and communications and serious environmental problems. Moreover, sulfur compounds are strong catalytic toxic substances in account of which the use of hydrocarbon gases for energetic and technological purposes is limited. From above mentioned, a complete separation of hydrogen sulfide from oil gases and its refining is of great importance for attaining of environmental safety.

In industry one or another method is used for oxidation of hydrogen sulfide in gases depending on the concentration. If the concentration of H_2S > 10 wt. %, an oxidation in gaseous phase (method of Claus) is used; at hydrogen sulfide concentration up to 10 wt. %, an oxidation in liquid phase is more rational and at hydrogen sulfide content: 0.2-0.3 wt. %, solid adsorbents are used. Within recent years an alternative methods of hydrogen sulfide utilization are considered more commonly which provide a production of hydrogen, available for energetic purposes together with sulfur. One of the promising methods involves the thermal catalytic decay of hydrogen sulfide at the temperatures higher than 370-380 ^{o}C. Oxides of vanadium, nickel, cobalt and manganese are recommended as catalysts for this process.[4-5]

In chemical industry an absorbers, prepared from zinc oxide, are mainly used for cleaning of synthesis-gas from sulfur compounds. Results of executed thermodynamic and experimental investigations confirm that, except from zinc oxide, active catalysts-adsorbents for H_2S utilization may be produced from manganese oxides, too. It is important also, that zinc and manganese sulfides are characterized by high stability even at small partial pressures of hydrogen.

Existing methods for gas cleaning from hydrogen sulfide are rated to large volumes. By opinion of specialists, for small and medium deposits of oil gases so-called block-modulus plants are considerably more efficient which are successfully promoted in various countries: Germany, China, Brazil, Russia and etc. At such plants a solid adsorbents are used. Iron-manganese concentrates of Baltic Sea, recommended for gas cleaning, contain 10-23 wt. % of manganese, nearly 25-27 % of iron and other compounds. Adsorbents of such type are the particles of irregular spheric shape of 5.0-50.0 mm size and have various fractional compositions. Use of solid adsorbents, instead of liquid ones, excludes an existence of harmful wastes of the production. Cleaned gas is a raw material for gas generator plants and is an ecologically pure natural gas for various technological purposes.[1] Previously the systematic investigations were carried out on the use of manganese catalysts in chemical industry[6] and for solving of ecological problems.[7] In the papers[8] the adsorbents of sulfur, based on low-grade manganese ores, were investigated and proposed for practical use. The concentrate of manganese natural ore (CMNO) was tested on critical and total sulfur content (Fig.1).

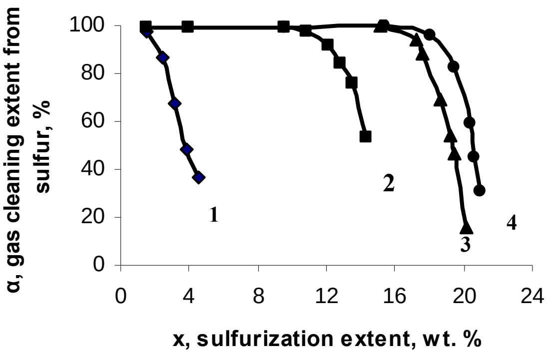

Figure 1. Dependence of the extent of gas cleaning from sulfur (α) on the extent of sulfurization of CMNO (X) at various temperatures: 1-200 °C; 2-300 °C; 3-370 °C; 4-415 °C. (Gas volume rate – 1000 h^{-1}; CS_2 concentration- 40 g m^{-3} by sulfur).

The logarithmic dependence of the fraction of residual sulfur in a gas on an extent of mass sulfurization can be described by equation:

$$\lg a = \lg a_0 + BX \quad (1)$$

where a - is a fraction of residual sulfur in a gas at the degree of mass sulfurization, X;

a_0– is a fraction of residual sulfur in a gas in the presence of fresh adsorbent;

B- is a constant.

The plot of the dependence of lg a on **X** is linear, the slope of which is equal to B and the portion, cutted from an ordinate by straight line, gives lg α_o , that is to say, a fraction of residual sulfur in a gas, in the presence of fresh adsorbent (Fig.2). Calculated value of activation energy of the process of gas cleaning from CS_2 in the range of temperature from 200 °C to 400 °C comprises 5 kcal mol^{-1}, indicative of diffusion character of the process.

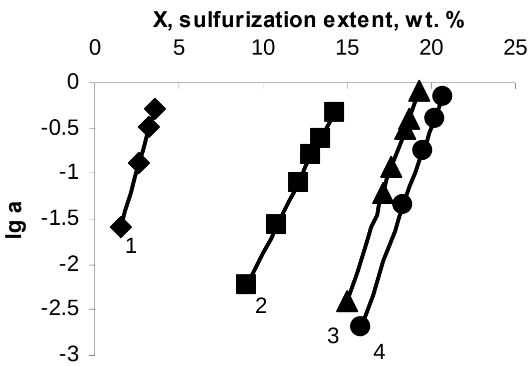

Figure 2. The logarithmic dependence of the fraction of residual sulfur in a gas (lg a) on an extent of mass sulfurization (X) for the process of gas cleaning from CS_2 at various temperatures, °C: 1 – 200; 2 – 300; 3 – 370; 4 – 415.

The dependence of critical sulfur content of CMNO on temperature at cleaning of nitrogen-hydrogen mixture from carbon disulfide and hydrogen sulfide has shown (Fig. 3) that with increasing of temperature the critical sulfur content of the mass by sulfur is enhanced. At temperature of 200 °C an overshoot of carbon disulfide is observed. At temperature of 290-300 °C an overshoot of CS_2, as well as of H_2S takes place nearly simultaneously. At temperature of 350 °C an overshoot of H_2S is proceeded at early stage, but degree of gas cleaning from CS_2 is maintained up to 95-96 %, for a long time.[9]

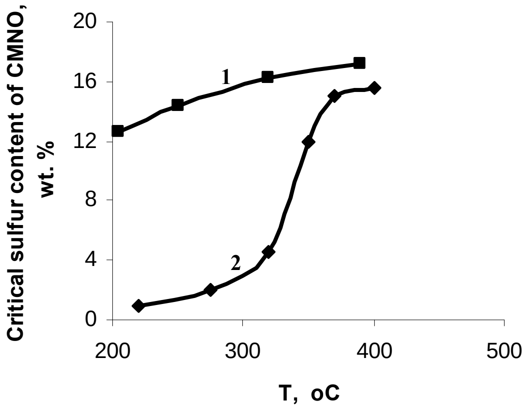

Figure 3. Dependence of critical sulfur content of CMNO on temperature at cleaning of nitrogen- hydrogen mixture (H_2:N_2=3:1) from H_2S (1) and CS_2 (2).

An analysis of scientific publications permits to note positive sides of the use of solid adsorbents, obtained from manganese natural ores in sulfur cleaning processes: sufficiently large sulfur capacity – up to 15.0 wt. %, cheapness and ecologically pure industrial wastes.

The following moments may be listed as negative ones:

Inspite of the efficiency, a wide practical use of such catalysts in modern high-technology processes is limited by their insufficient operating characteristics: small specific surface, low mechanical and thermal stability, single use of a mass.

The aim of presented work involves: the study of the process of cleaning of hydrocarbon gases by the concentrates of manganese natural ores (Chiatura deposit, Georgia) from sulfur compounds, an analysis of the reasons of limited utility of massive (carrier- less) oxide-manganese catalysts-adsorbents in industry and an advisability of elaboration of pilled compositions on their basis with optimal physical-chemical characteristics. The technology for preparation of pilled catalysts from the powders, containing manganese oxides, is proposed. An activation of prepared tablets was studied in the process of cleaning of natural gas from hydrogen sulfide. An effect of the parameters of pilling process: compacting pressure, composition, type and properties of stabilizing components on the formation of secondary structure was determined. Some physical-chemical characteristics of the pills are presented. A pilot lot of manganese catalyst- adsorbent was manufactured by elaborated technology at rotor pilling machine of two-way filling. It was shown that pilled oxide-manganese catalysts-adsorbents by total and critical sulfur content, mechanical strength and thermal stability, as well as by availability of initial raw material is competitive with some well-known types of zinc-containing adsorbents used in the industry.

Experimentals

Sample preparation.

The concentrates of manganese natural ores of Chiatura deposit (Georgia) were used for preparation of the tablets. Chemical composition of initial concentrates before and after reducing by nitrogen-hydrogen mixture at 650-700 °C for 2 h is presented in Table 1.

Table 1. Chemical composition of the concentrates of manganese oxide ores (wt. %)

№	MnO_2	MnO	SiO_2	Al_2O_3	Fe_2O_3	CaO
I	20.0-92.0	--	2.0-45.0	2.0-10.0	1.5-5.0	2.5-20.0
II	1.0-3.0	30.0-90.0	2.0-25.0	2.0-13.0	1.5-5.0	2.5-25.0

I-Initial sample; **II-** Reduced by nitrogen-hydrogen mixture at 650-700 °C, 2 h.

Table 2. Effect of phase composition of manganese oxides on mechanical strength of the tablets

Sample composit-ion, wt. %	Mechanical strength of the pills at compacting pressure, kg cm^{-2}		
	50	100	150
I - 10.0MnO, 80.0($CaO.2Al_2O_3$), 10.0H_2O	55.0	60.0	75.0
The same as I, reduced by H_2 at 400-450 °C, 2 h	50.0-60.0	55.0-60.0	70-75
II-80.0MnO_2, 10.0($CaO.2Al_2O_3$), 10.0H_2O	50.0	60.0	70.0-80.0
The same as II, reduced by H_2 at 400-450 °C, 2 h	-	-	-

Granulometric composition of initial and reduced manganese concentrates is roughly the same and comprises 0.05-0.1 mm. The mixture of the oxides of calcium and aluminum was used as a binder. Moisture content in a charge was varied from 5.0 to 15.0 wt. %. Laboratory mechanical press was used for tableting. Compacting pressure – 50, 100, 150 kg cm^{-2}. Pellets size ф = 8÷9 mm, height – *h* = 5÷6 mm.

Methods

The porosimeters of low and high pressure - MA-3M-1 were used to determine the mean radius and volume of the pores of the samples of oxide-manganese catalysts-adsorbents. Desulfurization process was studied at flouring plant. Methane was used as cleanable gas. A gas, after passing a flow meter, was entered in a saturator, where was saturated by a steam thereafter into a vessel by reaction:

$$BaS+2H_2O = Ba(OH)_2 + H_2S \qquad (2)$$

A gas was enriched by hydrogen sulfide and was headed into a reactor for cleaning. Quartz tube of 20 mm diameter and of 250 mm length was used as a reactor. It was equipped by Ni-Cr alloy spiral for heating. Gas analysis before and after reactor was carried out by the method of iodometric titration.

Results and Discussion

In Table 2 the data on mechanical strength of the pellets, prepared from initial and preliminary reduced concentrates of manganese ores, are given. The pellets prepared from the powders of manganese ores without reduction, as well as of reduced by hydrogen, are characterized by high mechanical strength. The pellets, prepared from non-reduced concentrates (simple II), in contrast of simple I, are decomposed in the form of fine powder after reducing by nitrogen-hydrogen mixture at 400-450 °C (2 hours).

With increasing of compacting pressure of the pellets, a significant variation of porous structure is observed. The pellets, prepared at low pressure (50 kg cm^{-2}), have the same volume of the pores V= 0.285 cm^3 g^{-1}. This index for the pellets, prepared at compacting pressures – 100 and 150 kg cm^{-2}, comprises 0.195 and 0.142 cm^3 g^{-1}, respectively (Table 3).

Table 3. Dependence of variation of some parameters of the tabletes on the value of compacting pressure at mechanical hand-operated pump

Sam-ples	Compacting pressure, P, kg cm^{-2}	Total volume of pores, cm^3 g^{-1}	Specific surface *S*, m^2 g^{-1}	Density g cm^{-3}
I	50	0.2854	7.7	2.3
II	100	0.1958	9.1	2.5
III	150	0.1413	22.33	2.7
Pilot	70-75	0.1848	49.75	2.5-2.8

Testing of the pellets in the course of cleaning of natural gas from hydrogen sulfide has shown that with increasing of temperature a sulfur content of a catalyst-adsorbent is increasing at an instant of overshoot of hydrogen sulfide (Fig. 4). Total sulfur content of pellets after 500 hours operation attains 18-20 wt. %.

Table 4. Some physical-chemical characteristics of pilot lot of pelleted oxide-manganese catalyst-adsorbent (pellet size *D*=9 mm, height *h*=5 mm)

Radius of pores			Total volume of pores, $cm^3 g^{-1}$	Specific surface, $m^2 g^{-1}$	Mechanical strength, $kg\ cm^{-2}$	Bulk density, $kg\ dm^{-3}$
r < 100Å	*r*-100-1000 Å	*r* >1000 Å				
80 ÷100	250 ÷750	3500÷5000	0.28-0.30	40.0– 50.0	80.0-90.0	1.6-1.8

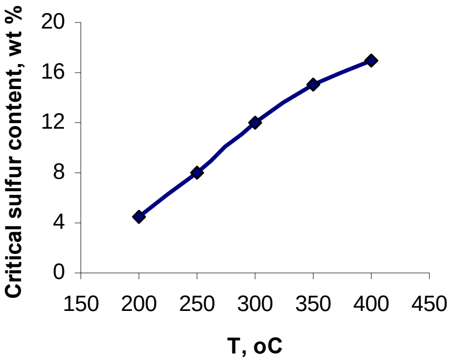

Figure 4. Dependence of critical sulfur content of pelleted manganese catalyst-adsorbent on the temperature at cleaning of methane from H_2S (V_{cat}=10 ml, G_{cat}=16g, W=1000 h^{-1}, flow rate of H_2S – 180 mg h^{-1} by sulfur, particle size comprises 1/4 part of whole granule).

High sulfur absorbance of manganese contacts in reducing medium may be explained by an ability of manganese oxides for stopping of reducing processes at the stage of sulfide formation. Because of this fact they are different from iron oxides in which the process is proceeded up to the formation of metallic iron. Cubic structures of Mn (II) oxide and of sulfide - MnS close by parameters, are favourable to total sulfurization of the oxides of Mn (II) and Mn (III):

Parameters	MnO	MnS
a, Å	4.436	5.611

Pilot lot of oxide-manganese catalyst - adsorbent in amount of 30 kg was manufactured by elaborated technology[10] at rotor pelletizing machine of two-way filling (Table 4). The prepared pellets, are characterized by a totality of the pores of various radius. Along with it, the main part involves the pores of low and medium radius.

The phase composition of pilot sample of sulfided oxide-manganese catalyst-adsorbent was studied by the thermal and X-ray diffraction methods. It was shown that in the temperature range of 300-700 °C an intensive oxidation of sulfide sulfur occurs. Manganese lower valence sulphur oxyacid salts of various compositions may be formed as the products of oxidation. End product of oxidation, manganese sulfate with an impurity of manganese sulfide begins to dissociate at the temperatures of 800-850 °C.

Conclusions

Performed investigation has shown that pelleted oxide-manganese catalyst-adsorbent absorbs efficiently a sulfur at cleaning of natural gas from H_2S in temperature range from 350 °C to 400 °C. Critical sulfur content comprises 15-17 wt. s%. Pellets of oxide-manganese catalyst-adsorbent, prepared by elaborated method, by its activity, absorbance and operating regime is in good competition with some types of zinc-containing adsorbent and by mechanical strength and thermal stability has the better indexes.

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